

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



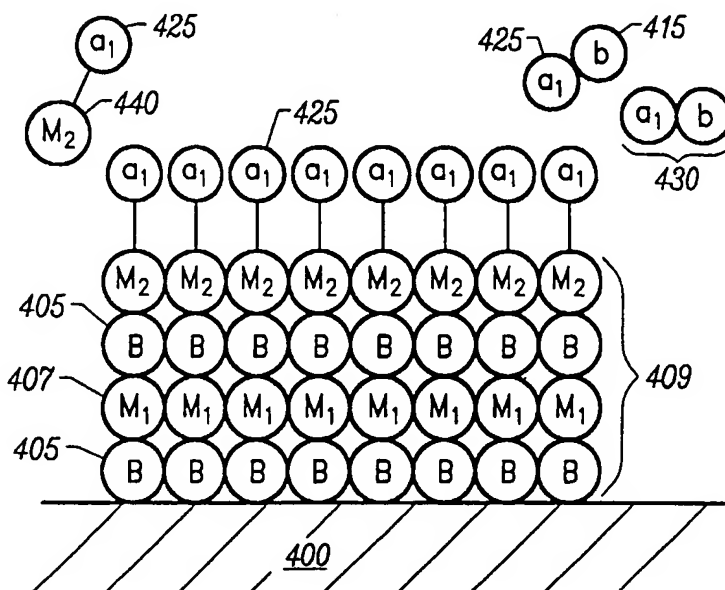
(43) International Publication Date  
3 January 2002 (03.01.2002)

PCT

(10) International Publication Number  
**WO 02/01628 A2**

- (51) International Patent Classification<sup>7</sup>: **H01L 21/768** (74) Agent: **BROOKS, Kenneth, C.**; Law Office of Kenneth C. Brooks, P.O. Box 10417, Austin, TX 78766-1417 (US).
- (21) International Application Number: **PCT/US01/20310**
- (22) International Filing Date: **26 June 2001 (26.06.2001)**
- (25) Filing Language: **English**
- (26) Publication Language: **English**
- (30) Priority Data:  
09/604,943 27 June 2000 (27.06.2000) **US**
- (71) Applicant: **APPLIED MATERIALS, INC.** [US/US];  
3050 Bowers Avenue, Santa Clara, CA 95050 (US).
- (72) Inventors: **BYUN, Jeong, Soo**; 2097 Valley Green Drive  
#257, Cupertino, CA 95014 (US). **MAK, Alfred, W.**;  
32722 Fellows Court, Union City, CA 94587 (US).
- (81) Designated States (*national*): **CN, JP, KR.**
- (84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).
- Published:  
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **FORMATION OF BORIDE BARRIER LAYERS USING CHEMISORPTION TECHNIQUES**



(57) Abstract: A method of forming a boride layer for integrated circuit fabrication is disclosed. In one embodiment, the boride layer is formed by chemisorbing monolayers of a boron-containing compound and one refractory metal compound onto a substrate. In an alternate embodiment, the boride layer has a composite structure. The composite boride layer structure comprises two or more refractory metals. The composite boride layer is formed by sequentially chemisorbing monolayers of a boron compound and two or more refractory metal compounds on a substrate.

WO 02/01628 A2

- 1 -

## FORMATION OF BORIDE BARRIER LAYERS USING CHEMISORPTION TECHNIQUES

### 5 BACKGROUND OF THE INVENTION

The present invention relates to the formation of boride barrier layers and, more particularly to boride barrier layers using chemisorption techniques.

In the manufacture of integrated circuits, barrier layers are often used to inhibit the diffusion of metals and other impurities into regions underlying such  
10 barrier layers. These underlying regions may include transistor gates, capacitor dielectric, semiconductor substrates, metal lines, as well as many other structures that appear in integrated circuits.

For the current subhalf-micron ( $0.5\ \mu\text{m}$ ) generation of semiconductor devices, any microscopic reaction at an interface between interconnection layers can  
15 cause degradation of the resulting integrated circuits (e.g., increase the resistivity of the interconnection layers). Consequently, barrier layers have become a critical component for improving the reliability of interconnect metallization schemes.

Compounds of refractory metals such as, for example, nitrides, borides, and carbides have been suggested as diffusion barriers because of their  
20 chemical inertness and low resistivities (e.g., resistivities typically less than about  $200\ \mu\Omega\text{-cm}$ ). In particular, borides such as, for example, titanium diboride ( $\text{TiB}_2$ ) have been suggested for use as a barrier material since layers formed thereof generally have low resistivities (e.g., resistivities less than about  $150\ \mu\Omega\text{-cm}$ ).

Boride barrier layers are typically formed using chemical vapor  
25 deposition (CVD) techniques. For example, titanium tetrachloride ( $\text{TiCl}_4$ ) may be reacted with diborane ( $\text{B}_2\text{H}_6$ ) to form titanium diboride ( $\text{TiB}_2$ ) using CVD. However, when Cl-based chemistries are used to form boride barrier layers, reliability problems can occur. In particular, boride layers formed using CVD chlorine-based chemistries typically have a high chlorine (Cl) content (e.g., chlorine content greater than about  
30 3%). A high chlorine content is undesirable because the chlorine may migrate from the boride barrier layer into adjacent interconnection layers, which can increase the contact resistance of such interconnection layers and potentially change the characteristics of integrated circuits made therefrom.

- 2 -

Therefore, a need exists in the art for reliable boride barrier layers for integrated circuit fabrication. Particularly desirable would be reliable boride barrier layers useful for interconnect structures.

5 SUMMARY OF THE INVENTION

Boride barrier layers for integrated circuit fabrication are provided. In one embodiment, the boride barrier layer comprises one refractory metal. The boride barrier layer may be formed by sequentially chemisorbing alternating monolayers of a boron compound and a refractory metal compound onto a substrate.

10 In an alternate embodiment, a composite boride barrier layer is formed. The composite boride barrier layer comprises two or more refractory metals. The composite boride barrier layer may be formed by sequentially chemisorbing monolayers of a boron compound and two or more refractory metal compounds onto a substrate.

15 The boride barrier layer is compatible with integrated circuit fabrication processes. In one integrated circuit fabrication process, the boride barrier layer comprises one refractory metal. The boride barrier layer is formed by sequentially chemisorbing alternating monolayers of a boron compound and one refractory metal compound on a substrate. Thereafter, one or more metal layers are  
20 deposited on the boride barrier layer to form an interconnect structure.

In another integrated circuit fabrication process, the boride barrier layer has a composite structure. The composite boride barrier layer comprises two or more refractory metals. The composite boride barrier layer is formed by sequentially chemisorbing monolayers of a boron compound and two or more refractory metal  
25 compounds on a substrate. Thereafter, one or more metal layers are deposited on a composite boride barrier layer to form an interconnect structure.

BRIEF DESCRIPTION OF THE DRAWINGS

The teachings of the present invention can be readily understood by considering the following detailed description in conjunction with the accompanying  
30 drawings, in which:

Fig. 1 depicts a schematic illustration of an apparatus that can be used for the practice of embodiments described herein;

- 3 -

Figs. 2a-2c depict cross-sectional views of a substrate structure at different stages of integrated circuits fabrication incorporating a boride barrier layer;

Figs. 3a-3c depict cross-sectional views of a substrate undergoing a first sequential chemisorption process of a boron compound and one refractory metal compound to form a boride barrier layer;

Figs. 4a-4d depict cross-sectional views of a substrate undergoing a second sequential chemisorption process of a boron compound and two refractory metal compounds to form a composite boride barrier layer;

Figs. 5a-5d depict cross sectional views of a substrate undergoing a third sequential chemisorption of a boron compound and two refractory metal compounds to form a composite boride barrier layer; and

Figs. 6a-6c depict cross-sectional views of a substrate structure at different stages of integrated circuit fabrication incorporating more than one boride barrier layer.

15

#### DETAILED DESCRIPTION OF THE INVENTION

Fig. 1 depicts a schematic illustration of a wafer processing system 10 that can be used to form boride barrier layers in accordance with embodiments described herein. The system 10 comprises a process chamber 100, a gas panel 130, a control unit 110, along with other hardware components such as power supplies 106 and vacuum pumps 102. The salient features of process chamber 100 are briefly described below.

##### Chamber 100

The process chamber 100 generally houses a support pedestal 150, which is used to support a substrate such as a semiconductor wafer 190 within the process chamber 100. Depending on the specific process, the semiconductor wafer 190 can be heated to some desired temperature prior to layer formation.

In chamber 100, the wafer support pedestal 150 is heated by an embedded heater 170. For example, the pedestal 150 may be resistively heated by applying an electric current from an AC power supply 106 to the heater element 170.

- 4 -

The wafer 190 is, in turn, heated by the pedestal 150, and can be maintained within a desired process temperature range of, for example, about 20°C to 500°C.

A temperature sensor 172, such as a thermocouple, is also embedded in the wafer support pedestal 150 to monitor the temperature of the pedestal 150 in a conventional manner. For example, the measured temperature may be used in a feedback loop to control the electric current applied to the heater element 170 by the power supply 106, such that the wafer temperature can be maintained or controlled at a desired temperature that is suitable for the particular process application. The pedestal 150 is optionally heated using radiated heat (not shown).

A vacuum pump 102 is used to evacuate process gases from the process chamber 100 and to help maintain the desired pressure inside the chamber 100. An orifice 120 is used to introduce process gases into the process chamber 100. The dimensions of the orifice 120 are variable and typically depend on the size of the process chamber 100.

The orifice 120 is coupled to a gas panel 130 via a valve 125. The gas panel 130 provides process gases from two or more gas sources 135 and 136 to the process chamber 100 through orifice 120 and valve 125. The gas panel 130 also provides a purge gas from a purge gas source 138 to the process chamber 100 through orifice 120 and valve 125.

A control unit 110, such as a computer, controls the flow of various process gases through the gas panel 130 as well as valve 125 during different steps of a wafer process sequence. Illustratively, the control unit 110 comprises a central processing unit (CPU) 112, support circuitry 114, and memories containing associated control software 116. In addition to the control of process gases through the gas panel 130, the control unit 110 is also responsible for automated control of the numerous steps required for wafer processing, such as wafer transport, temperature control and chamber evacuation, among other steps.

The control unit 110 may be one of any form of general-purpose computer processor that can be used in an industrial setting for controlling various chambers and sub-processors. The computer processor may use any suitable memory, such as random access memory, read only memory, floppy disk drive, hard disk, or any other form of digital storage, local or remote. Various support circuits may be

- 5 -

coupled to the computer processor for supporting the processor in a conventional manner. Software routines as required may be stored in the memory or executed by a second processor that is remotely located. Bi-directional communications between the control unit 110 and the various components of the wafer processing system 10 are  
5 handled through numerous signal cables collectively referred to as signal buses 118, some of which are illustrated in Fig. 1.

#### Boride Barrier Layer Formation

Figs. 2a-2c illustrate one preferred embodiment of boride layer  
10 formation for integrated circuit fabrication of an interconnect structure. In general, the substrate 200 refers to any workpiece upon which film processing is performed, and substrate structure 250 is used generally to denote the substrate 200 as well as other material layers formed on the substrate 200. Depending on the specific stage of processing, the substrate 200 may be a silicon semiconductor wafer, or other material  
15 layer, which has been formed on the wafer. Fig. 2a, for example, shows a cross-sectional view of a substrate structure 250, having a material layer 202 thereon. In this particular illustration, the material layer 202 may be an oxide (e.g. silicon dioxide). The material layer 202 has been conventionally formed and patterned to provide a contact hole 202H extending to the top surface 200T of the substrate 200.

20 Fig. 2b shows a boride layer 204 conformably formed on the substrate structure 250. The boride layer 204 is formed by chemisorbing monolayers of a boron containing compound and refractory metal compound on the substrate structure 250.

The monolayers are chemisorbed by sequentially providing a boron-containing compound and one or more refractory metal compounds to a process  
25 chamber. In a first sequential chemisorption process, the monolayers of the boron containing compound and one refractory metal compound are alternately chemisorbed on a substrate 300 as shown in Figs. 3a-3c.

Fig. 3a depicts a cross-sectional view of a substrate 300, which may be in a stage of integrated circuit fabrication. A monolayer of a boron-containing  
30 compound 305 is chemisorbed on the substrate 300 by introducing a pulse of a boron containing gas into a process chamber similar to that shown in Fig. 1. The boron-containing compound typically combines boron atoms 310 with one or more reactive

- 6 -

species b 315. During boride layer formation, the reactive species b 315 form byproducts that are transported from the substrate 300 surface by the vacuum system.

The chemisorbed monolayer of the boron-containing compound 305 is self-limiting in that only one monolayer may be chemisorbed onto the substrate 300 surface during a given pulse. Only one monolayer of the boron-containing compound is chemisorbed on the substrate because the substrate has a limited surface area. This limited surface area provides a finite number of sites for chemisorbing the boron-containing compound. Once the finite number of sites are occupied by the boron-containing compound, further chemisorption of the boron-containing compound will be blocked.

The boron-containing compound may be, for example, a borane compound having the general formula  $B_xH_y$ , where x has a range between 1 and 10, and y has a range between 3 and 30. For example, borane ( $BH_3$ ), diborane ( $B_2H_6$ ), triborane ( $B_3H_9$ ), tetraborane ( $B_4H_{12}$ ), pentaborane ( $B_5H_{15}$ ), hexaborane ( $B_6H_{18}$ ), heptaborane ( $B_7H_{21}$ ), octaborane ( $B_8H_{24}$ ), nanoborane ( $B_9H_{27}$ ), and decaborane ( $B_{10}H_{30}$ ), may be used as the boron-containing compound.

After the monolayer of the boron compound is chemisorbed onto the substrate 300, excess boron containing compound is removed from the process chamber by introducing a pulse of a purge gas thereto. Purge gases such as, for example, helium (He), argon (Ar), nitrogen ( $N_2$ ), ammonia ( $NH_3$ ), and hydrogen ( $H_2$ ), among others may be used.

After the process chamber has been purged, a pulse of one refractory metal compound is introduced into the process chamber. Referring to Fig. 3b, a layer of the refractory metal compound 307 is chemisorbed on the boron monolayer 305. The refractory metal compound typically combines refractory metal atoms 320 with one or more reactive species a 325.

The chemisorbed monolayer of the refractory metal compound 307 reacts with the boron-containing monolayer 305 to form a boride layer 309. The reactive species a 325 and b 315 form byproducts ab 330 that are transported from the substrate 300 surface by the vacuum system. The reaction of the refractory metal compound 307 with the boron monolayer 305 is self-limited, since only one monolayer of the boron compound was chemisorbed onto the substrate 300 surface.

- 7 -

The refractory metal compound may include refractory metals such as, for example, titanium (Ti), tungsten (W), tantalum (Ta), zirconium (Zr), hafnium (Hf), molybdenum (Mo), niobium (Nb), vanadium (V), and chromium (Cr), among others combined with reactive species such as, for example, chlorine (Cl) and fluorine (F). For example, titanium tetrachloride ( $\text{TiCl}_4$ ), tungsten hexafluoride ( $\text{WF}_6$ ), tantalum pentachloride ( $\text{TaCl}_5$ ), zirconium tetrachloride ( $\text{ZrCl}_4$ ), hafnium tetrachloride ( $\text{HfCl}_4$ ), molybdenum pentachloride ( $\text{MoCl}_5$ ), niobium pentachloride ( $\text{NbCl}_5$ ), vanadium pentachloride ( $\text{VCl}_5$ ), chromium tetrachloride ( $\text{CrCl}_4$ ) may be used as the refractory metal compound.

After the monolayer of the refractory metal compound is chemisorbed onto the substrate 300, any excess refractory metal compound is removed from the process chamber by introducing another pulse of the purge gas therein. Thereafter, as shown in Fig. 3c, the boride layer deposition sequence of alternating monolayers of the boron-containing compound and the refractory metal compound are repeated until a desired boride layer thickness is achieved. The boride layer may, for example, have a thickness in the range of 200 Å to about 5000 Å, and more preferably about 2500 Å.

In Figs. 3a-3c, boride layer formation is depicted as starting with the chemisorption of a boron-containing monolayer on the substrate followed by a monolayer of a refractory metal compound. Alternatively, the boride layer formation may start with the chemisorption of a monolayer of a refractory metal compound on the substrate followed by a monolayer of the boron-containing compound.

The pulse time for each pulse of the boron-containing compound, the one or more refractory metal compounds, and the purge gas is variable and depends on the volume capacity of the deposition chamber as well as the vacuum system coupled thereto. Similarly, the time between each pulse is also variable and depends on the volume capacity of the process chamber as well as the vacuum system coupled thereto.

In general, the alternating monolayers may be chemisorbed at a substrate temperature less than about 500°C, and a chamber pressure less than about 100 torr. A pulse time of less than about 1 second for the boron-containing compound, and a pulse time of less than about 1 second for the refractory metal compound are typically sufficient to chemisorb the alternating monolayers that comprise the boride



- 8 -

layer on the substrate. A pulse time of less than about 1 second for the purge gas is typically sufficient to remove the reaction byproducts as well as any residual materials remaining in the process chamber.

In a second chemisorption process, the boron containing monolayers  
5 and two or more refractory metal compounds are alternately chemisorbed on the substrate to form a composite boride layer. Fig. 4a depicts a cross-sectional view of a substrate 400, which may be in a stage of integrated circuit fabrication. A self-limiting monolayer of a boron-containing compound 405 is chemisorbed on the substrate 400 by introducing a pulse of a boron-containing compound into a process chamber  
10 similar to that shown in Fig 1 according to the process conditions described above with reference to Figs. 2a-2c. The boron-containing compound combines boron atoms 410 with one or more reactive species b 415.

After the monolayer of the boron compound 405 is chemisorbed onto the substrate 400, excess boron containing compound is removed from the process  
15 chamber by introducing a pulse of purge gas thereto.

Referring to Fig 4b, after the process chamber has been purged, a pulse of a first refractory metal compound  $M_1a_1$  is introduced into the process chamber. A layer of the first refractory metal compound 407 is chemisorbed on the boron monolayer 405. The first refractory metal compound typically combines first  
20 refractory metal atoms  $M_1$  420 with one or more reactive species  $a_1$  425.

The chemisorbed monolayer of the first refractory metal compound 407 reacts with the boron-containing monolayer 405 to form a boride monolayer 409. The reactive species  $a_1$  425 and b 415 form byproducts  $a_1b$  430 that are transported from the substrate 400 surface by the vacuum system.

25 After the monolayer of the first refractory metal compound 407 is chemisorbed onto the substrate 400, the excess first refractory metal compound  $M_1a_1$  is removed from the process chamber by introducing another pulse of the purge gas therein.

Another pulse of the boron-containing compound is then introduced  
30 into the process chamber. A monolayer of the boron containing compound 405 is chemisorbed on the first refractory metal monolayer 407, as shown in Fig. 4c. The chemisorbed monolayer of the boron-containing compound 405 reacts with the first

- 9 -

refractory metal monolayer 407 to form a boride layer 409. The reactive species  $a_1$  425 and  $b$  415 form byproducts  $a_1b$  430 that are transported from the substrate 400 surface by the vacuum system.

After the monolayer of the boron compound 405 is chemisorbed onto  
5 the first refractory metal monolayer 407, excess boron containing compound is removed from the process chamber by introducing a pulse of a purge gas thereto.

Referring to Fig.4d, after the process chamber has been purged, a pulse of a second refractory metal compound  $M_2a_1$  is introduced into the process chamber. A layer of the second refractory metal compound 411 is chemisorbed on the boron  
10 monolayer 405. The second refractory metal compound typically combines second refractory metal atoms  $m_2$  440 with one or more reactive species  $a_1$  425.

The chemisorbed monolayer of the second refractory metal compound 411 reacts with the boron-containing monolayer 405 to form the boride composite layer 409. The reactive species  $a_1$  425 and  $b$  415 form byproducts  $a_1b$  430 that are  
15 transported from the substrate 400 surface by the vacuum system.

After the monolayer of the second refractory metal compound 411 is chemisorbed onto the substrate 400, the excess second refractory metal compound  $M_2a_1$  is removed from the process chamber by introducing another pulse of a purge gas therein.

20 Thereafter, the boride layer deposition sequence of alternating monolayers of the boron containing compound and the two refractory metal compounds  $M_1a_1$  and  $M_2a_1$  are repeated until a desired boride layer thickness is achieved.

In Figs. 4a-4d, boride layer formation is depicted as starting with the  
25 chemisorption of the boron containing monolayer on the substrate followed by monolayers of the two refractory metal compounds. Alternatively, the boride layer formation may start with the chemisorption of the monolayers of either of the two refractory metal compounds on the substrate followed by monolayers of the boron-containing compound. Optionally, monolayers of more than two refractory metal  
30 compounds may be chemisorbed on the substrate 400.

- 10 -

In a third chemisorption process, the boron containing monolayers and two or more refractory metal compounds are alternately chemisorbed on the substrate to form a composite boride layer, as illustrated in Fig 5a-5d.

Fig. 5a depicts a cross-sectional view of a substrate 500, which may be in a stage of integrated circuit fabrication. A self-limiting monolayer of a first refractory metal compound 507 is chemisorbed on the substrate 500 by introducing a pulse of a first refractory metal compound  $M_1a_1$  into a process chamber similar to that shown in Fig 1 according to the process conditions described above with reference to Figs. 2a-2c.

After the monolayer of the first refractory metal compound 507 is chemisorbed onto the substrate 500, excess first refractory metal compound is removed from the process chamber by introducing another pulse of the purge gas thereto.

Referring to Fig.5b, after the process chamber has been purged, a pulse of a second refractory metal compound  $M_2a_1$  is introduced into the process chamber. A layer of the second refractory metal compound 511 is chemisorbed on the first refractory metal monolayer 507.

After the monolayer of the second refractory metal compound 511 is chemisorbed onto the substrate 500, the excess second refractory metal compound  $M_2a_1$  is removed from the process chamber by introducing another pulse of the purge gas therein.

A pulse of the boron-containing compound is then introduced into the process chamber. A monolayer of the boron containing compound 505 is chemisorbed on the second refractory metal monolayer 511, as shown in Fig. 5c. The chemisorbed monolayer of the boron-containing compound 505 reacts with the second refractory metal monolayer 511 to form a boride layer 509. The reactive species  $a_1$  525 and  $b$  515 form byproducts  $a_1b$  530 that are transported from the substrate 500 surface by the vacuum system.

After the monolayer of the boron compound 505 is chemisorbed onto the second refractive metal monolayer 511, excess boron containing compound is removed from the process chamber by introducing a pulse of a purge gas thereto.

- 11 -

Referring to Fig.5d, after the process chamber has been purged, a pulse of a first refractory metal compound  $M_1a_1$  is introduced into the process chamber. A monolayer of the first refractory metal compound 507 is chemisorbed on the boron monolayer 505.

5           The chemisorbed monolayer of the first refractory metal compound 507 reacts with the boron-containing monolayer 505 to form a boride monolayer 509. The reactive species  $a_1$  525 and  $b$  515 form byproducts  $a_1b$  530 that are transported from the substrate 500 surface by the vacuum system.

          After the monolayer of the first refractory metal compound 507 is  
10 chemisorbed onto the substrate 500, the excess first refractory metal compound  $M_1a_1$  is removed from the process chamber by introducing another pulse of a purge gas therein.

          Thereafter, the boride layer deposition sequence of alternating monolayers of the boron containing compound and the two refractory metal  
15 compounds  $M_1a_1$  and  $M_2a_1$  are repeated until a desired boride layer thickness is achieved.

          In Figs. 5a-5d, boride layer formation is depicted as starting with the chemisorption of the first refractory metal monolayer on the substrate followed by monolayers of the second refractory metal compound and the boron-containing  
20 compound. Alternatively, the boride layer formation may start with the chemisorption of the monolayer of the boron-containing compound on the substrate followed by the monolayers of the two refractory metal compounds. Optionally, monolayers of more than two refractory metal compounds may be chemisorbed on the substrate 500.

          The sequential deposition processes described above advantageously  
25 provide good step coverage for the boride layer, due to the monolayer chemisorption mechanism used for forming the boride layer. In particular, boride layer formation using the monolayer chemisorption mechanism is believed to contribute to a near perfect step coverage over complex substrate topographies.

          Furthermore, in chemisorption processes, since only one monolayer  
30 may be absorbed on the topographic surface, the size of the deposition area is largely independent of the amount of the amount of precursor gas remaining in the reaction chamber once the monolayer has been formed.

- 12 -

Referring to Fig. 2c, after the formation of the boride layer 204, a contact layer 206 may be formed thereon to complete the interconnect structure. The contact layer 206 is preferably selected from the group of aluminum (Al), copper (Cu), tungsten (W), and combinations thereof.

5           The contact layer 206 may be formed, for example, using chemical vapor deposition (CVD), physical vapor deposition (PVD), or a combination of both CVD and PVD. For example, an aluminum (Al) layer may be deposited from a reaction of a gas mixture containing dimethyl aluminum hydride (DMAH) and hydrogen (H<sub>2</sub>) or argon (Ar) or other DMAH containing compounds, a CVD copper  
10   layer may be deposited from a gas mixture containing Cu<sup>+2</sup> (hfac)<sub>2</sub> (copper hexafluoro acetylacetonate), Cu<sup>+2</sup> (fod)<sub>2</sub> (copper heptafluoro dimethyl octanediene), Cu<sup>+1</sup> hfac TMVS (copper hexafluoro acetylacetonate trimethylvinylsilane), or combinations thereof, and a CVD tungsten layer may be deposited from a gas mixture containing tungsten hexafluoride (WF<sub>6</sub>). A PVD layer is deposited from a copper target, an  
15   aluminum target, or a tungsten target.

Figs. 6a-6c illustrate an alternate embodiment of boride layer formation for integrated circuit fabrication of the interconnect structure. In general, the substrate 600 refers to any workpiece upon which film processing is performed, and a substrate structure 650 is used generally to denote the substrate 600 as well as  
20   other material layers formed on the substrate 600. Depending upon the specific stage of processing, the substrate 600 may be a silicon semiconductor wafer, or other material layer, which has been formed on the wafer. Fig. 6a, for example, shows a cross-sectional view of a substrate structure 650, having a material layer 602 thereon. In this particular illustration, the material layer 602 may be an oxide (e.g., silicon  
25   dioxide). The material layer 602 has been conventionally formed and patterned to provide a contact hole 602H extending to the top surface 600T of the substrate 600.

Fig. 6b shows two boride layers 604 and 606 conformably formed on the substrate structure 650. The boride layers 604 and 606 are formed by chemisorbing monolayers of a boron-containing compound and one or more  
30   refractory metal compounds on the substrate structure 650 as described above with reference to Fig. 3a-5d. The two boride layers 604 and 606 may each comprise one or more refractory metals. The thickness of the two or more boride layers 604 and 606

- 13 -

may be variable depending on the specific stage of processing. Each boride layer 604 and 606 may, for example, have a thickness in the range of about 200Å to 5000Å.

Referring to Fig. 6c, after the formation of the boride layers 604 and 606, a contact layer 608 may be formed thereon to complete the interconnect structure. The contact layer 608 is preferably selected from the group of aluminum (Al), copper (Cu), tungsten (W), and combinations thereof.

The specific process conditions disclosed in the above discussion are meant for illustrative purposes only. Other combinations of process parameters such as precursor and inert gases, flow ranges, pressure and temperature may also be used in forming the boride layer of the present invention.

Although several preferred embodiments, which incorporate the teaching of the present inventions, have been shown and described in detail, those skilled in the art can readily devise many other varied embodiments that still incorporate these teachings.

- 14 -

WHAT IS CLAIMED IS:

1                   1.     A method of film deposition for integrated circuit fabrication,  
2     comprising the step of:

3                   (a) forming at least one boride layer on a substrate, wherein the at  
4     least one boride layer is formed using a sequential chemisorption process.

1                   2.     The method of claim 1 wherein the at least one boride layer  
2     comprises one or more refractory metals.

1                   3.     The method of claim 2 wherein the one or more refractory  
2     metals are selected from the group of titanium (Ti), tungsten (W), vanadium (V),  
3     niobium (Nb), tantalum (Ta), zirconium (Zr), hafnium (Hf), chromium (Cr), and  
4     molybdenum (Mo).

1                   4.     The method of claim 1 wherein the sequential chemisorption  
2     process of step (a) comprises the step of:

3                   (b) chemisorbing monolayers of a boron-containing compound and  
4     one or more refractory metal compounds on the substrate to form the boride layer  
5     thereon.

1                   5.     The method of claim 4 wherein the substrate is subjected to a  
2     purge gas following chemisorption of each monolayer.

1                   6.     The method of claim 4 wherein the boron-containing  
2     compound has the general formula  $B_xH_y$ , where x has a range between 1 and 10, and y  
3     has a range between 3 and 30.

1                   7.     The method of claim 6 wherein the boron-containing  
2     compound is selected from the group of borane ( $BH_3$ ), diborane ( $B_2H_6$ ), triborane  
3     ( $B_3H_9$ ), tetraborane ( $B_4H_{12}$ ), pentaborane ( $B_5H_{15}$ ), hexaborane ( $B_6H_{18}$ ), heptaborane  
4     ( $B_7H_{21}$ ), octaborane ( $B_8H_{24}$ ), nanoborane ( $B_9H_{27}$ ), and decaborane ( $B_{10}H_{30}$ ).

- 15 -

1                   8.     The method of claim 4 wherein one or more of the refractory  
2 metal compounds are selected from the group of titanium tetrachloride ( $\text{TiCl}_4$ ),  
3 tungsten hexafluoride ( $\text{WF}_6$ ), tantalum pentachloride ( $\text{TaCl}_5$ ), zirconium tetrachloride  
4 ( $\text{ZrCl}_4$ ), hafnium tetrachloride ( $\text{HfCl}_4$ ), molybdenum pentachloride ( $\text{MoCl}_5$ ), niobium  
5 pentachloride ( $\text{NbCl}_5$ ), vanadium chloride ( $\text{VCl}_x$ ), chromium chloride ( $\text{CrCl}_x$ )

1                   9.     The method of claim 4 wherein step (b) is performed at a  
2 temperature less than about  $500^\circ\text{C}$ .

1                   10.    The method of claim 4 wherein step (b) is performed at a  
2 pressure less than about 100 torr.

1                   11.    The method of claim 5 wherein purge gas is selected from the  
2 group of helium (He), argon (Ar), hydrogen ( $\text{H}_2$ ), nitrogen ( $\text{N}_2$ ), ammonia ( $\text{NH}_3$ ), and  
3 combinations thereof.

1                   12.    The method of claim 4 wherein monolayers of the boron-  
2 containing compound and the one or more refractory metal compounds are alternately  
3 chemisorbed on the substrate.

1                   13.    The method of claim 12 wherein one monolayer of the boron-  
2 containing compound is chemisorbed between each chemisorbed monolayer of the  
3 one or more refractory metal compounds.

1                   14.    The method of claim 12 wherein one monolayer of the boron-  
2 containing compound is chemisorbed on the substrate after two or more monolayers  
3 of the one or more refractory metal compounds are chemisorbed thereon.



- 16 -

- 1                   15.     A method of forming a barrier layer structure for use in  
2 integrated circuit fabrication, comprising the steps of:  
3                   (a) providing a substrate having an oxide layer thereon, wherein the  
4 oxide layer has apertures formed therein to a top surface of the substrate; and  
5                   (b) forming at least one boride layer on at least portions of the oxide  
6 layer and the substrate surface, wherein the at least one boride layer is formed using a  
7 sequential chemisorption process.
- 1                   16.     The method of claim 15 wherein the at least one boride layer  
2 comprises one or more refractory metals.
- 1                   17.     The method of claim 16 wherein the one or more refractory  
2 metals are selected from the group of titanium (Ti), tungsten (W), vanadium (V),  
3 niobium (Nb), tantalum (Ta), zirconium (Zr), hafnium (Hf), chromium (Cr), and  
4 molybdenum (Mo).
- 1                   18.     The method of claim 15 wherein the sequential chemisorption  
2 of step (b) comprises the step of:  
3                   (b) chemisorbing monolayers of a boron-containing compound and  
4 one or more refractory metal compounds on the substrate to form the boride layer  
5 thereon.
- 1                   19.     The method of claim 18 wherein the substrate is subjected to a  
2 purge gas following chemisorption of each monolayer.
- 1                   20.     The method of claim 18 wherein the boron containing  
2 compound has the general formula  $B_xH_y$ , where x has a range between 1 and 10, and  
3 y has a range between 3 and 30.
- 1                   21.     The method of claim 20 wherein the boron-containing  
2 compound is selected from the group of borane ( $BH_3$ ), diborane ( $B_2H_6$ ), triborane  
3 ( $B_3H_9$ ), tetraborane ( $B_4H_{12}$ ), pentaborane ( $B_5H_{15}$ ), hexaborane ( $B_6H_{18}$ ), heptaborane  
4 ( $B_7H_{21}$ ), octaborane ( $B_8H_{24}$ ), nanoborane ( $B_9H_{27}$ ), and decaborane ( $B_{10}H_{30}$ ).

- 17 -

1                   22.    The method of claim 18 wherein the one or more refractory  
2 metal compounds are selected from the group of titanium tetrachloride ( $\text{TiCl}_4$ ),  
3 tungsten hexafluoride ( $\text{WF}_6$ ), tantalum pentachloride ( $\text{TaCl}_5$ ), zirconium tetrachloride  
4 ( $\text{ZrCl}_4$ ), hafnium tetrachloride ( $\text{HfCl}_4$ ), molybdenum pentachloride ( $\text{MoCl}_5$ ), niobium  
5 pentachloride ( $\text{NbCl}_5$ ), vanadium chloride ( $\text{VCl}_x$ ), chromium chloride ( $\text{CrCl}_x$ )

1                   23.    The method of claim 18 wherein step (c) is performed at a  
2 temperature of less than about  $500^\circ\text{C}$ .

1                   24.    The method of claim 18 wherein step (c) is performed at a  
2 pressure of less than about 100 torr.

1                   25.    The method of claim 19 wherein the purge gas is selected from  
2 the group of helium (He), argon (Ar), hydrogen ( $\text{H}_2$ ), nitrogen ( $\text{N}_2$ ), ammonia ( $\text{NH}_3$ ),  
3 and combinations thereof.

1                   26.    The method of claim 18 wherein monolayers of the boron-  
2 containing compound and the one or more refractory metal compounds are alternately  
3 chemisorbed on the substrate.

1                   27.    The method of claim 26 wherein one monolayer of the boron-  
2 containing compound is chemisorbed between each chemisorbed monolayer of the  
3 one or more refractory metal compounds.

1                   28.    The method of claim 26 wherein one monolayer of the boron-  
2 containing compound is chemisorbed on the substrate after two or more monolayers  
3 of the one or more refractory metal compounds are chemisorbed thereon.

- 18 -

- 1                   29.    A method of forming a barrier layer structure for use in  
2   integrated circuit fabrication, comprising the steps of:  
3                   (a)   providing a substrate having an oxide layer thereon, wherein the  
4   oxide layer has apertures formed therein to a top surface of the substrate;  
5                   (b)   forming a first boride layer on at least portions of the oxide layers  
6   and the substrate surface, wherein the first boride layer comprises two or more  
7   refractory metals; and  
8                   (c)   forming a second boride layer on the first boride layer wherein the  
9   second boride layer comprises two or more refractory metals.
- 1                   30.    The method of claim 29 wherein the first boride layer has a  
2   thickness less than about 100Å (angstroms).
- 1                   31.    The method of claim 29 wherein the second boride layer has a  
2   thickness in the range of about 500Å to about 3000Å.
- 1                   32.    The method of claim 29 wherein the first boride layer and the  
2   second boride layer are each formed using a sequential chemisorption process.
- 1                   33.    The method of claim 32 wherein the sequential chemisorption  
2   process of step (a) comprises the step of:  
3                   (a)   chemisorbing monolayers of a boron-containing compound and  
4   one or more refractory metal compounds on the substrate.
- 1                   34.    The method of claim 33 wherein monolayers of the boron  
2   containing compound and the one or more refractory metal compounds are alternately  
3   chemisorbed on the substrate.
- 1                   35.    The method of claim 34 wherein one monolayer of the boron-  
2   containing compound is chemisorbed between each chemisorbed monolayer of the  
3   one or more refractory metal compounds.
- 1                   36.    The method of claim 34 wherein one monolayer of the boron-  
2   containing compound is chemisorbed on the substrate after two or more monolayers  
3   of the one or more refractory metal compounds are chemisorbed thereon.

- 19 -

1                   37.    A computer storage medium containing a software routine that,  
2   when executed, causes a general purpose computer to control the deposition chamber  
3   using a method of thin film deposition comprising the step of:

4                   (a) forming a boride layer on a substrate, wherein the boride layer is  
5   formed using a sequential chemisorption process.

1                   38.    The computer storage medium of claim 37 wherein the boride  
2   layer comprises one or more refractory metals.

1                   39.    The computer storage medium of claim 38 wherein the one or  
2   more refractory metals are selected from the group of titanium (Ti), tungsten (W),  
3   vanadium (V), niobium (Nb), tantalum (Ta), zirconium (Zr), hafnium (Hf), chromium  
4   (Cr), and molybdenum (Mo).

1                   40.    The computer storage medium of claim 37 wherein the  
2   sequential chemisorption process of step (a) comprises the step of:

3                   (a) chemisorbing monolayers of a boron-containing compound and  
4   one or more refractory metal compounds on the substrate to form the boride layer  
5   thereon.

1                   41.    The computer storage medium of claim 40 wherein the  
2   substrate is subjected to a purge gas following chemisorption of each monolayer.

1                   42.    The computer storage medium of claim 40 wherein the boron-  
2   containing compound has the general formula  $B_xH_y$ , where x has a range between 1  
3   and 10, and y has a range between 3 and 30.

1                   43.    The computer storage medium of claim 42 wherein the boron-  
2   containing compound is selected from the group of borane ( $BH_3$ ), diborane ( $B_2H_6$ ),  
3   triborane ( $B_3H_9$ ), tetraborane ( $B_4H_{12}$ ), pentaborane ( $B_5H_{15}$ ), hexaborane ( $B_6H_{18}$ ),  
4   heptaborane ( $B_7H_{21}$ ), octaborane ( $B_8H_{24}$ ), nanoborane ( $B_9H_{27}$ ), and decaborane  
5   ( $B_{10}H_{30}$ ).

- 20 -

1                   44.     The computer storage medium of claim 40 wherein the one or  
2     more refractory metal compounds are selected from the group of titanium  
3     tetrachloride ( $\text{TiCl}_4$ ), tungsten hexafluoride ( $\text{WF}_6$ ), tantalum pentachloride ( $\text{TaCl}_5$ ),  
4     zirconium tetrachloride ( $\text{ZrCl}_4$ ), hafnium tetrachloride ( $\text{HfCl}_4$ ), molybdenum  
5     pentachloride ( $\text{MoCl}_5$ ), niobium pentachloride ( $\text{NbCl}_5$ ), vanadium chloride ( $\text{VCl}_x$ ),  
6     chromium chloride ( $\text{CrCl}_x$ ).

1                   45.     The computer storage medium of claim 40 wherein monolayers  
2     of the boron-containing compound and the one or more refractory metal compounds  
3     are alternately chemisorbed on the substrate.

1                   46.     The computer storage medium of claim 45 wherein one  
2     monolayer of the boron-containing compound is chemisorbed between each  
3     chemisorbed monolayer of the one or more refractory metal compounds.

1                   47.     The computer storage medium of claim 45 wherein one  
2     monolayer of the boron-containing compound is chemisorbed on the substrate after  
3     two or more monolayers of the one or more refractory metal compounds are  
4     chemisorbed thereon

1                   48.     A device, comprising:  
2                   at least one boride layer formed on a substrate, wherein one of the at  
3     least one boride layers comprises two or more refractory metals.

1  
2                   49.     The device of claim 48 wherein the two or more refractory  
3     metals are selected from the group of titanium (Ti), tungsten (W), vanadium (V),  
4     niobium (Nb), tantalum (Ta), zirconium (Zr), hafnium (Hf), chromium (Cr), and  
5     molybdenum (Mo).

- 21 -

1                   50.    A device, comprising:  
2                   a substrate having an oxide layer thereon, wherein the oxide layer has  
3   apertures formed therein to a top surface of the substrate; and  
4                   at least one boride layer formed on portions of the oxide layers and the  
5   substrate surface, wherein one of the at least one boride layer comprises two or more  
6   refractory metals.

1                   51.    The device of claim 50 wherein the two or more refractory  
2   metals are selected from the group of titanium (Ti), tungsten (W), vanadium (V),  
3   niobium (Nb), tantalum (Ta), zirconium (Zr), hafnium (Hf), chromium (Cr), and  
4   molybdenum (Mo).

1                   52.    An interconnect structure, comprising:  
2                   a substrate having an oxide layer thereon, wherein the oxide layer has  
3   apertures formed therein to a top surface of the substrate; and  
4                   a first boride layer formed on portions of the oxide layers and the  
5   substrate surface, wherein the first boride layer comprises two or more refractory  
6   metals; and  
7                   a second boride layer the first boride layer wherein the second boride  
8   layer comprises one or more refractory metals

1                   53.    The interconnect structure of claim 52 wherein the one or more  
2   refractory metals are selected from the group of titanium (Ti), tungsten (W),  
3   vanadium (V), niobium (Nb), tantalum (Ta), zirconium (Zr), hafnium (Hf), chromium  
4   (Cr), and molybdenum (Mo).

1                   54.    The interconnect structure of claim 52 wherein the first boride  
2   layer has a thickness less than about 100Å (angstroms).

1                   55.    The interconnect structure of claim 52 wherein the second  
2   boride layer has a thickness in the range of about 500Å and 3000Å.

1/7

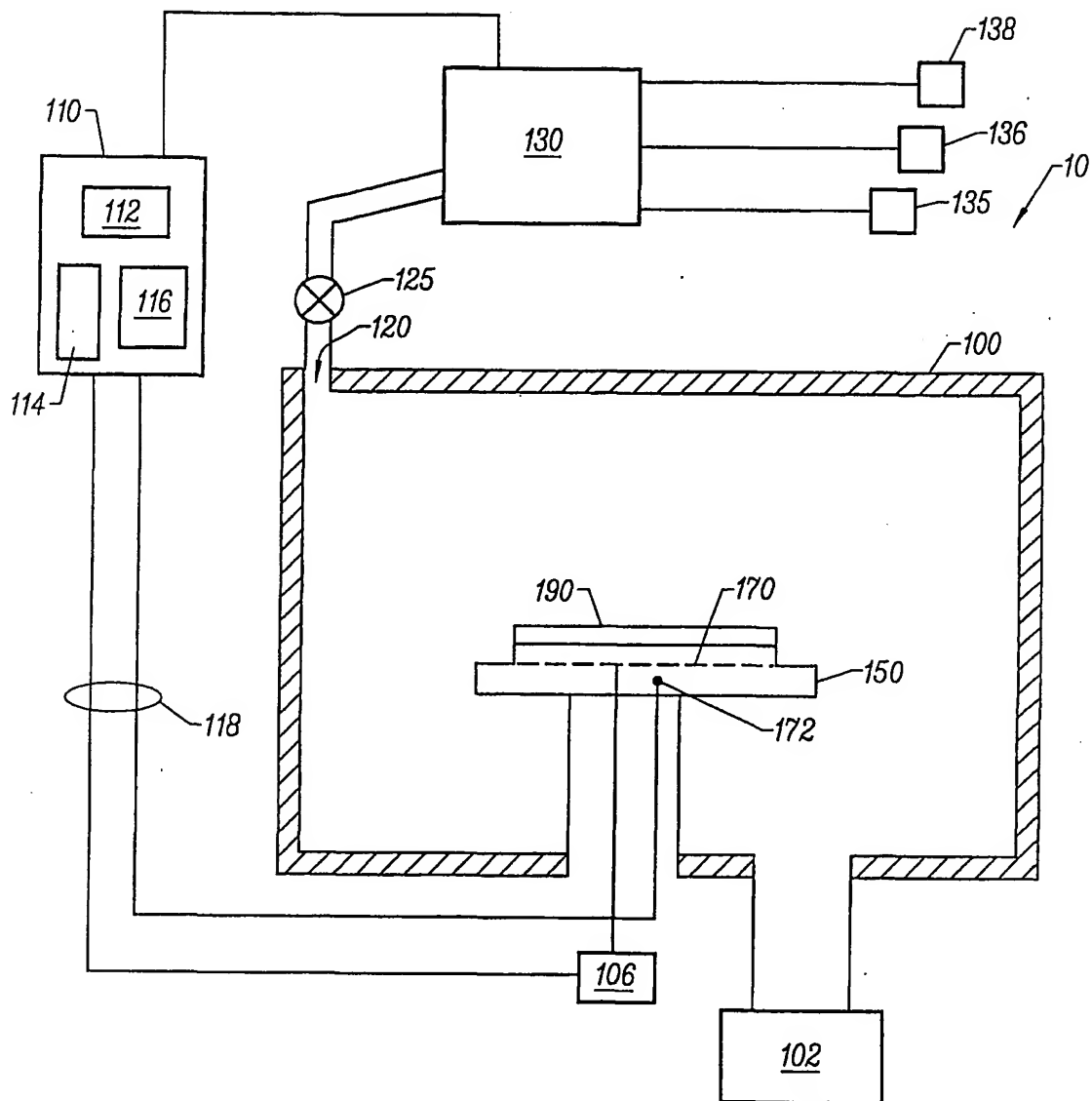


FIG. 1

2/7

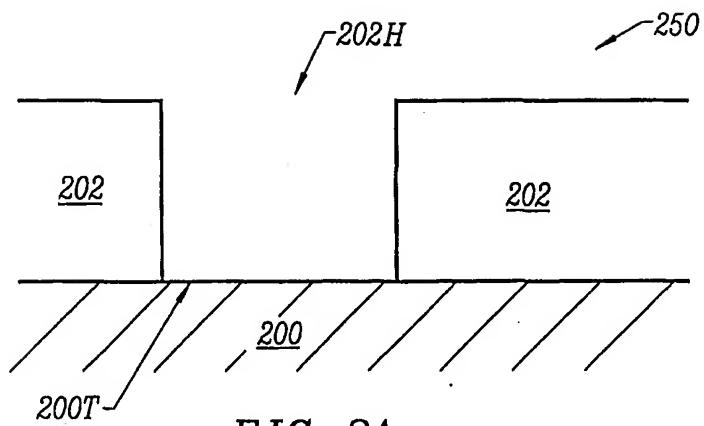


FIG. 2A

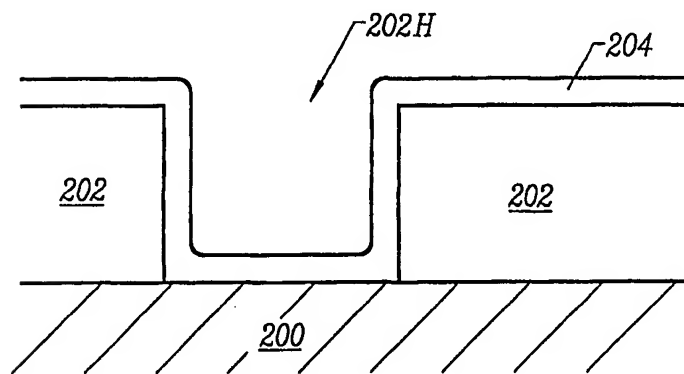


FIG. 2B

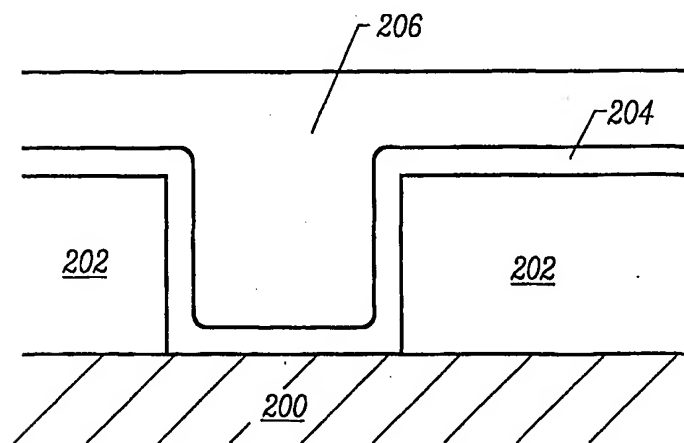


FIG. 2C



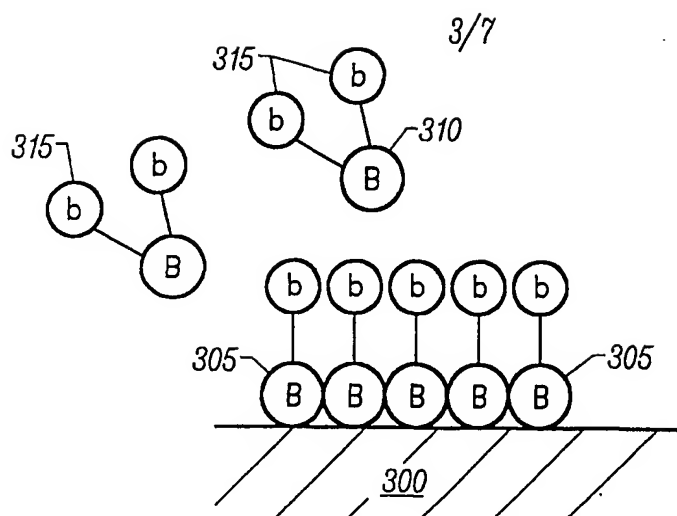


FIG. 3A

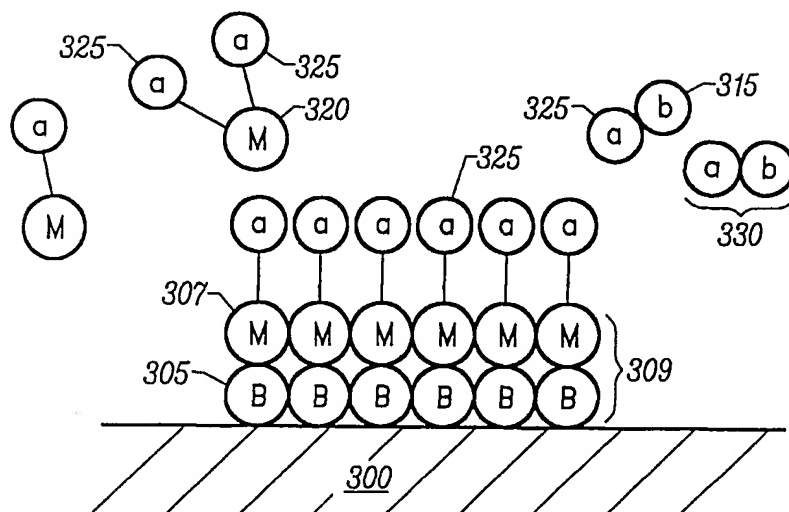


FIG. 3B

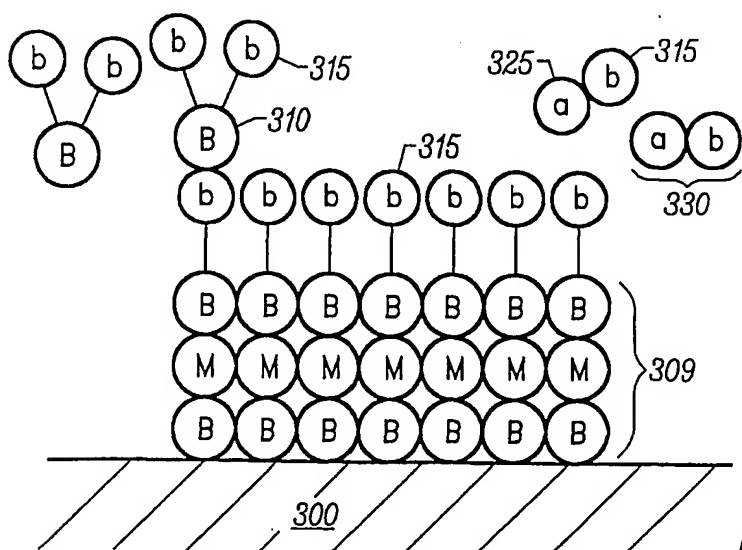
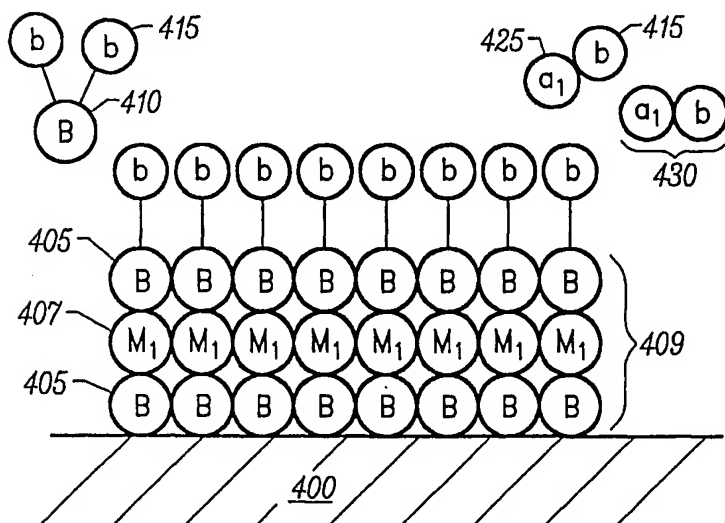
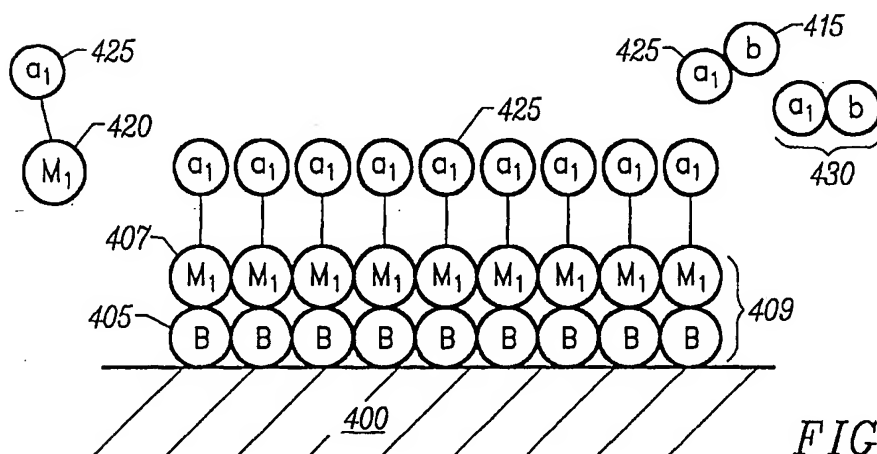
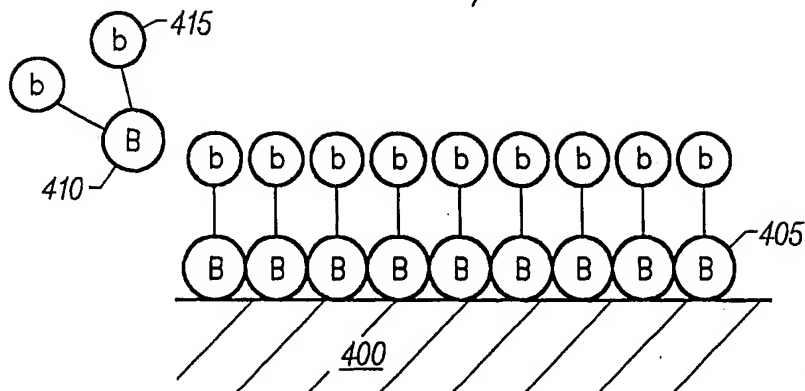


FIG. 3C

4/7



5/7

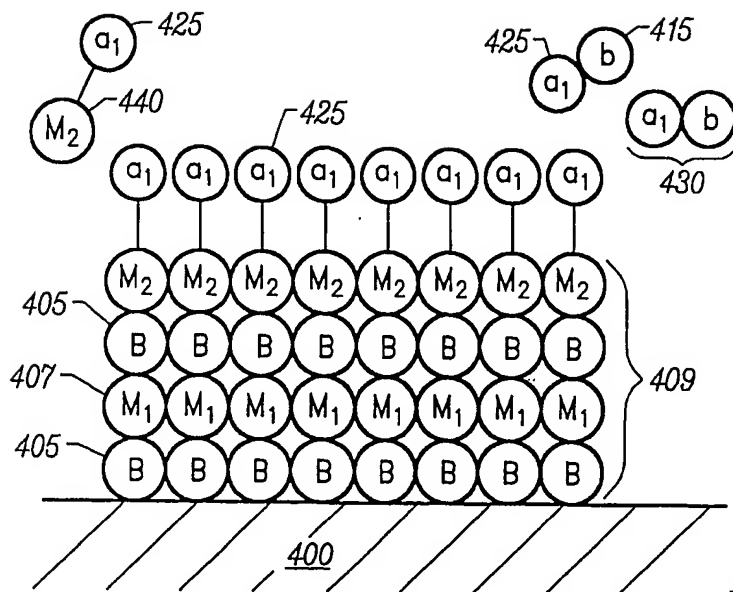


FIG. 4D

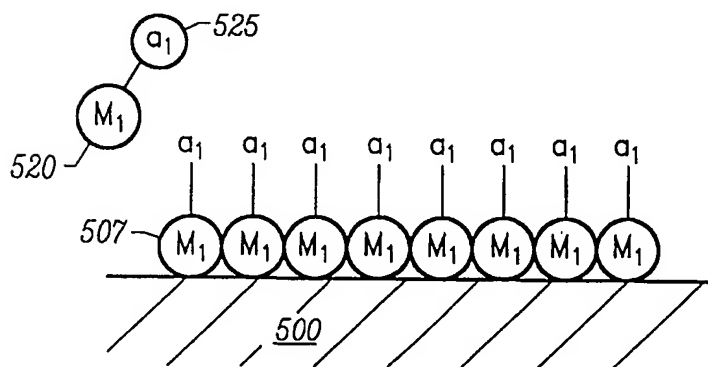


FIG. 5A

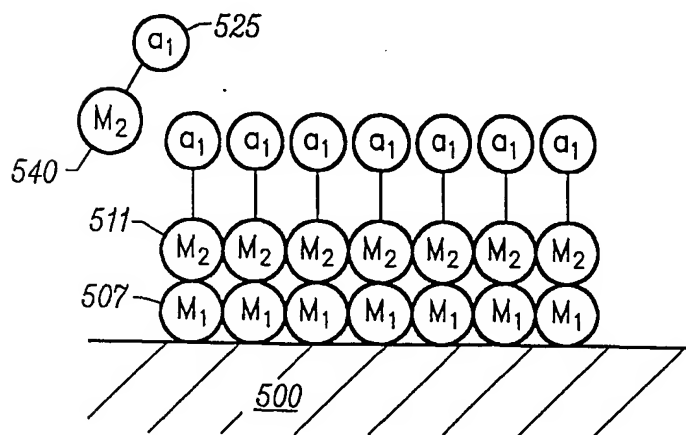
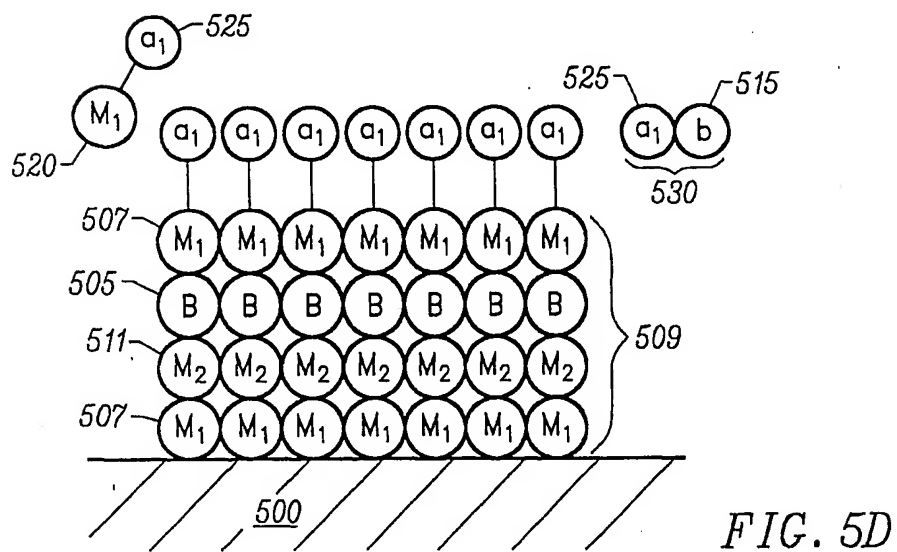
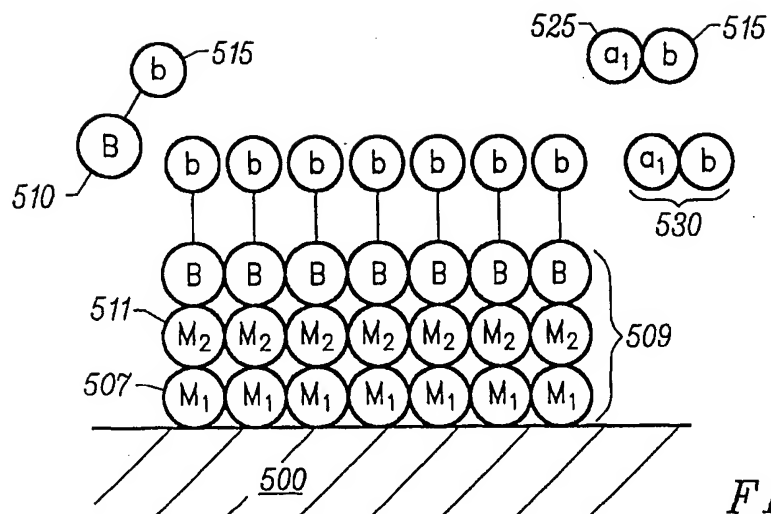
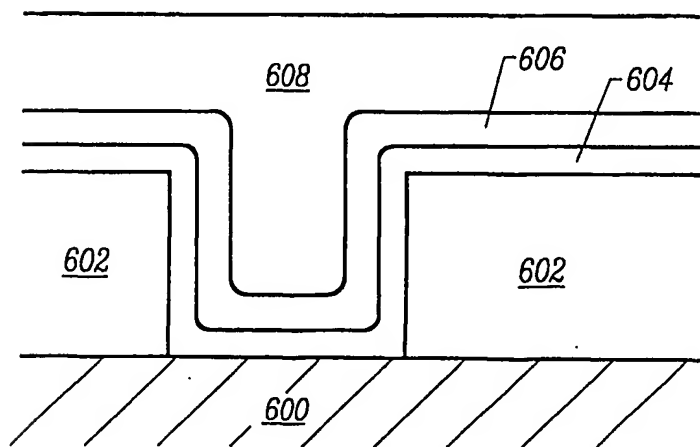
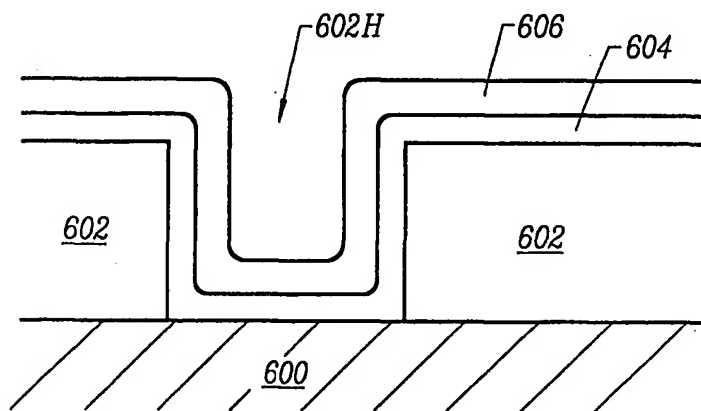
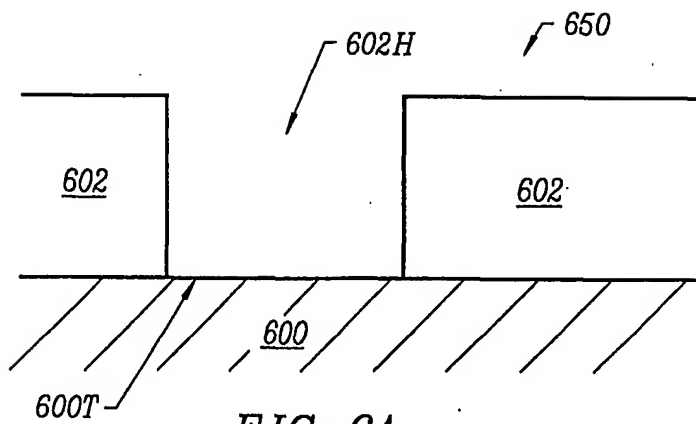


FIG. 5B

6/7



7/7



**THIS PAGE BLANK (USPTO)**